Supporting Information

Experimental Apparatus.

A photograph of the apparatus used for high temperature impedance characterization of pressed pellet samples is shown in Figure S1. The thermocouple passes through the bottom alumina disc and approaches the bottom platinum contact from the bottom up. Electrical connection to the bottom contact is made by the indicated Pt wire which was attached by welding. An internal Pt wire was welded to the Pt rod used to contact the top of the sample. A bushing (not visible) was used to load the visible spring to apply gentle force to the sample.

To confirm the repeatability of measurements, multiple samples of sodium exchanged zeolite X (Aldrich) were investigated, as producing a large quantity of VPI-9 is difficult. Figure S2 shows data from three Na-X samples prepared and characterized on different days (separated by weeks). Measured values of conductivity and observed trends are in accordance with other published literature.[1] All VPI-9 used in this study was from a pool of as-made material, produced from many identical synthesis batches. Each batch was crystallized according to a previously published method and as stated in the main article[2]; the crystalline product of each was confirmed by powder X-ray diffraction. Every batch appeared the same visually and by powder X-ray diffraction.

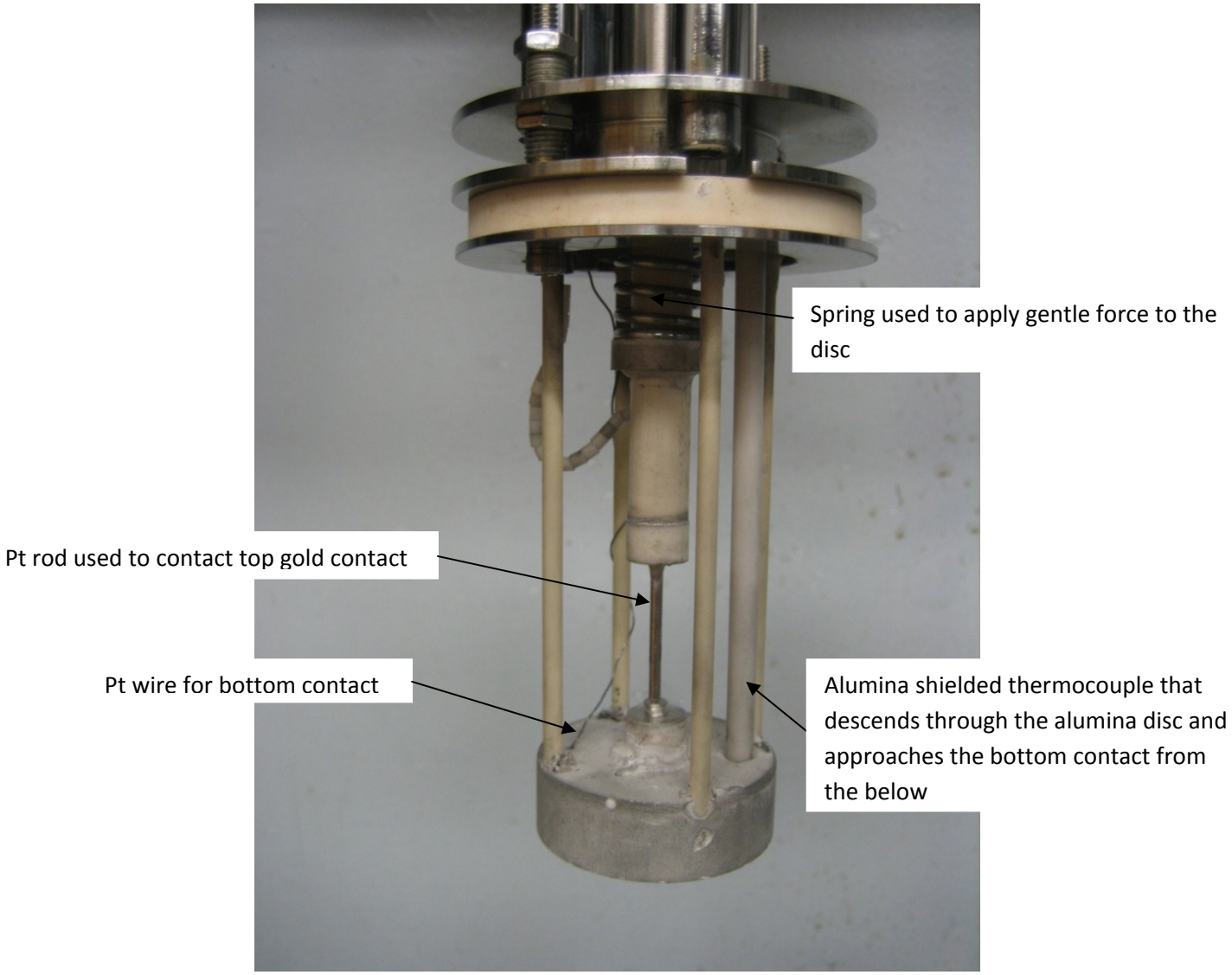

Figure S1. Experimental apparatus used for the high temperature characterization of pressed pellets.

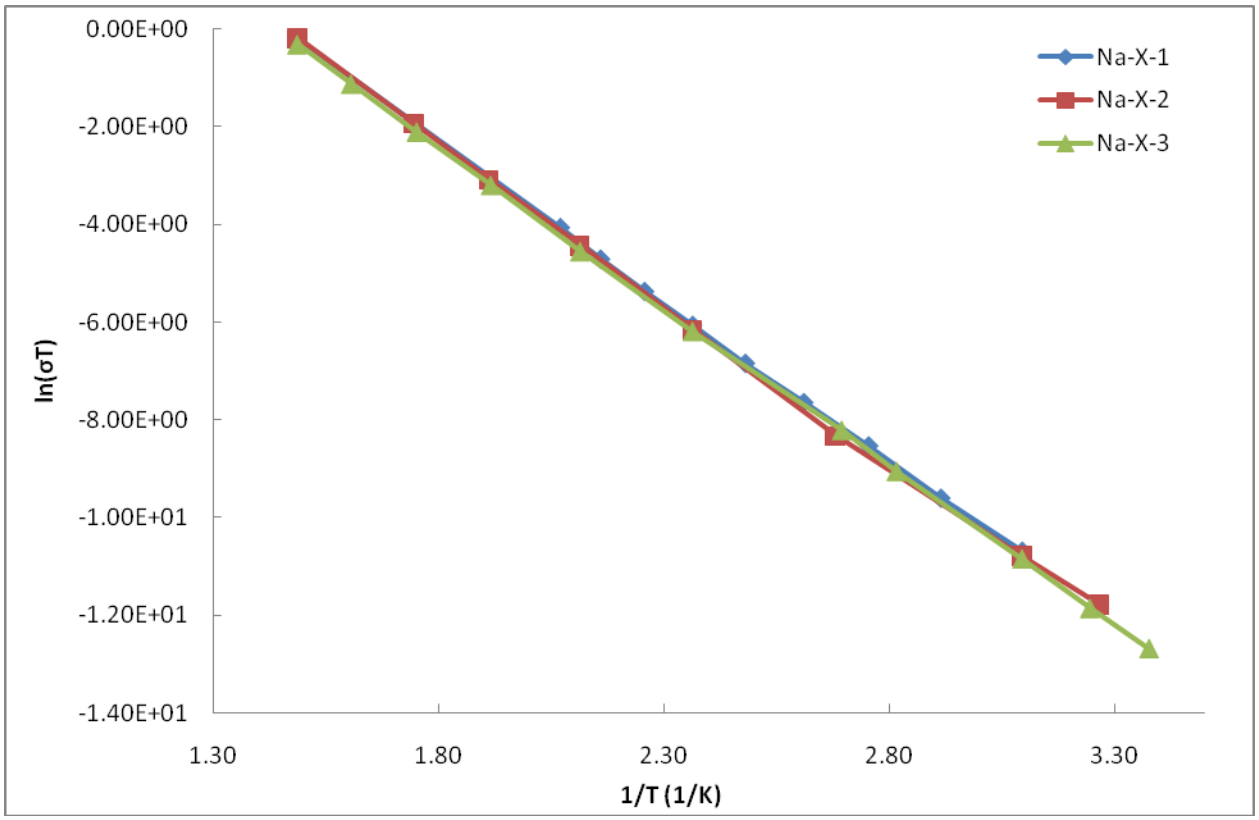

Figure S2. Conductivity data for three samples of Na-X. Pellets were all prepared following the same procedure described in the manuscript, but pellets were pressed on different days, contacts were sputtered in on different days, and characterization occurred on different days (separated in weeks, in fact).

A further discussion of impedance spectroscopy on zeolite samples.

In a series of papers on ionic motion in zeolites[3-6], it was suggested the presentation of data in the modulus representation, equation 1, and in particular the imaginary part of the modulus, M" as a function of frequency, rather than traditional impedance (Z) data, allowed for more straight forward visualization of ionic conduction and local relaxations. In equation S1, *i* is the square root of -1, ω is the frequency in radians per second, C_0 is the empty cell capacitance, M* is the complex modulus, and Z* is the complex impedance.

$$M^* = i\omega C_0 Z^* \qquad \text{S1)}$$

A further article on ion conductivity in ETS-10 also uses modulus representation, and presents data on sodium exchanged zeolite X and ETS-10.[7]

In our investigation of ionic conductivity in VPI-9, we began by first repeating literature results from the aforementioned papers on Na-X, but we found this to be a non-straightforward process. Figure S3 shows M" data from a pressed pellet of Na-X with sputtered gold contacts, recorded at 303 K.

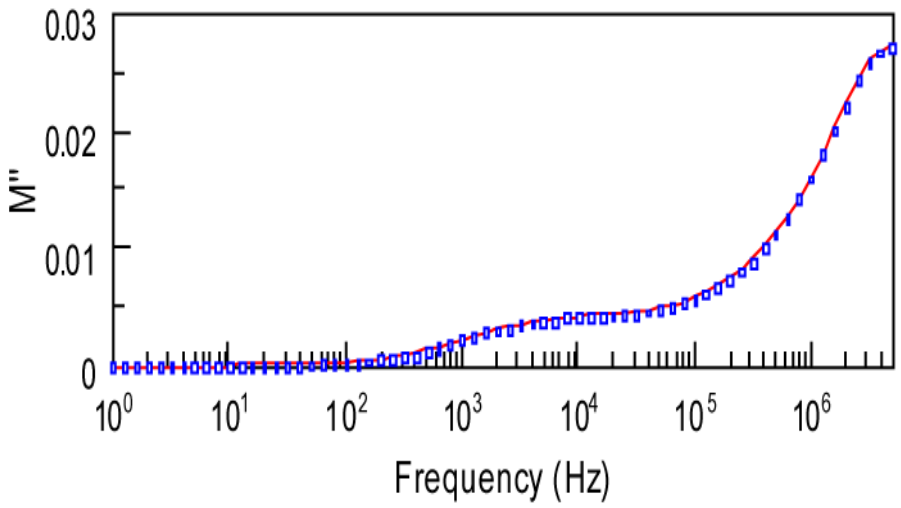

Figure S3. Imaginary part of the modulus as a function of frequency for a hydraulically pressed pellet of Na-X with sputtered gold contacts.

An intense peak at high frequency is clearly seen, which has been previously attributed to the local motion of a sodium ion within the large α cages in zeolite X.[6] The peak (or hump, rather) at low frequency, however is not well resolved from the large high frequency peak, as in references 4 and 6. This was troubling at first, but further experimentation revealed the answer. Figure S4 shows M" spectra of Na-X powder, held between two platinum discs in vacuum, at various temperatures, and in this case two well resolved peaks are observed. The low frequency peak has been attributed to the long range ionic conduction process[6], but the full interpretation is more complex, and will be discussed shortly. Finally, Figure S5 shows M" data for Na-X powder drop-cast from an ethanol slurry onto an interdigitated electrode (IE) structure (Novocontrol). The sample was dehydrated in vacuum to remove water and ethanol, and contributions to the spectra from the IE substrate have been subtracted. Again, two well resolved peaks are observed, with nearly equal peak heights. Pressed pellets of NaX without sputtered contacts were also characterized by directly sandwiching them between two

Pt electrodes, and spectra similar to those show in Figure S4, but with less peak separation, were observed.

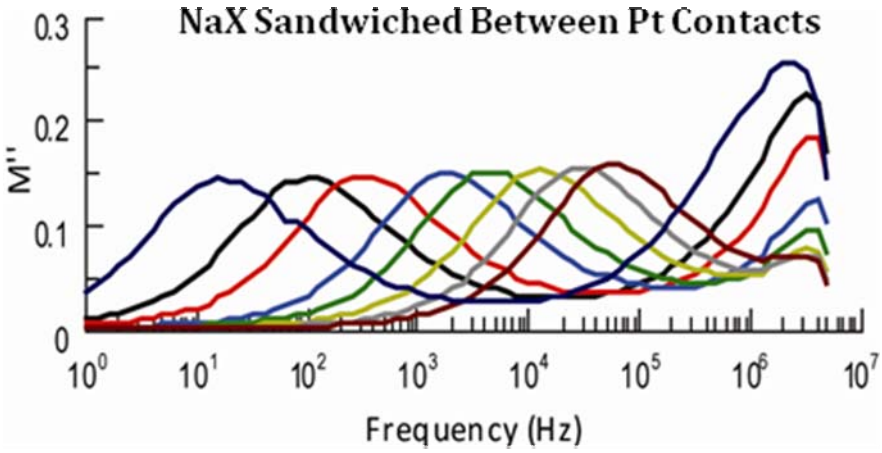

Figure S4. M" spectra of Na-X powder held between two circular Pt plates.

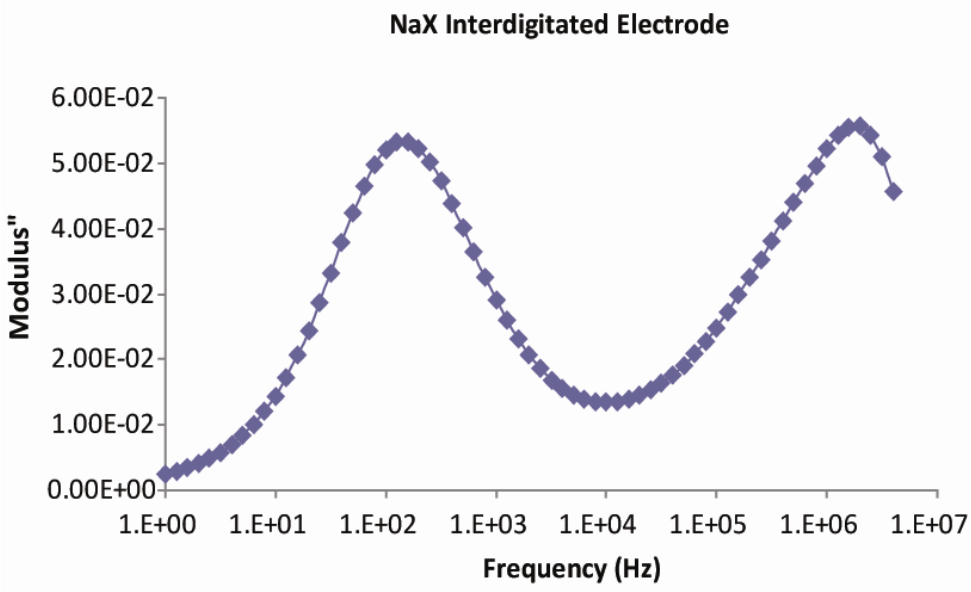

Figure S5. M" spectra for Na-X powder drop case from ethanol onto interdigitated electrode structure.

Circuit models are often used to describe the physical processes occurring in ionic conduction and the most common element is the parallel combination of a resistor and a capacitor. The M" spectra for Na-X can be modeled using two of these elements in series, one element corresponding to the motion of a sodium ion in an α cage and one to represent the long range process (such as DC conduction).[7]

To illustrate how circuit model parameter values (R_i and C_i) influence the fitting of data, and to help elucidate the nature of the variation in shape and position of the low frequency peak, Mathematica was used to plot M" as a function of frequency. This is shown in Figure S6, along with the circuit model used to generate the appropriate equations (by taking the laplace transform of the appropriate transfer function). In the M" spectra, each RC parallel element corresponds to one of the peaks.

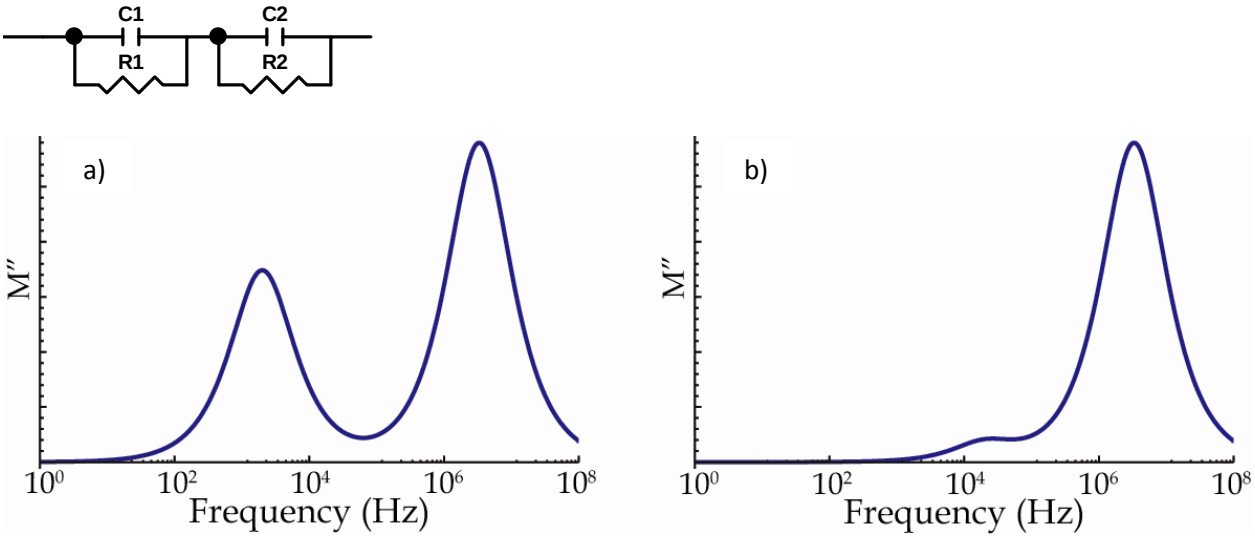

Figure S6. M" spectra calculated and plotted using Mathematica.

In both Figure S6 a) and b) R2 and C2 are held constant and correspond to the high frequency peak. In a), however, a smaller value of C1 and larger value of R1 are used than in b). The peak position in frequency is controlled by the value R1, larger

values of R1 shifting the peak to lower frequencies. The height of the peak is controlled by the value C1, smaller values of C1 increasing the peak height.

Recall that the M” spectra for a pressed pellet with sputtered contacts looks like Figure S6 b) while spectra of Na-X powder held between two Pt plates, Na-X powder drop cast onto IE electrodes, and pressed pellets of Na-X without sputtered electrodes more closely resemble Figure S6 a). Poor interparticle contact, particularly in the non-hydraulically pressed powder samples and poor particle contact with the electrodes in all three latter cases significantly increase the value of R1, which can be thought of as an overall resistance of the sample (corresponding to long range ionic conductivity in the absence of these parasitic effects). The increase in R1 causes peak separation in frequency. In the latter three cases C1, some overall capacitance, decreases with the addition of more series capacitors arising from an increase in space between particles and poor interfacial contact with the gold or platinum electrodes.

It should be noted that the high frequency peak in Na-X samples appears at the same frequency for a give temperature for all methods of characterization, indicating a true internal process, as was previously suggested.[6] Interestingly, VPI-9 samples do not show multiple peaks at any temperature in the M” spectra when powder samples are sandwiched between Pt plates, suggesting the absence of internal relaxation processes.

While presenting data in M” representation is useful for over emphasizing high frequency data and, therefore, studying internal processes that may occur very quickly, eliminating parasitic impedances by pressing pellets and forming intimate electrical

contacts is more appropriate for extracting values of ionic conductivity. (Nearly all reviewed literature on solid electrolytes reports on sintering powders and either painting on metallic contacts from Pt paste or using a physical vapor deposition technique to apply intimate metallic contacts.)

The characterization of powder samples between two circular Pt electrodes was accomplished by replacing the long Pt probe used to contact the top of pelltized samples (see Figure S1) with an alumina tube with a flat Pt disc attached to the bottom. A piece of quartz tube having an internal diameter the same as the external diameter of the Pt plates/alumina tube was used to hold the powder in place while sandwiching between Pt contacts. This is similar to what was done in reference 5.

References

(1) Kalogeras, I. M.; Vassilikou-Dova, A. *Defect and Diffusion Forum* **1998**, *164*, 1.

(2) McCusker, L. B.; Grosse-Kunstleve, R. W.; Baerlocher, C.; Yoshikawa, M.; Davis, M. E. *Microporous Materials* **1996**, *6*, 295.

(3) Franke, M. E.; Simon, U. *Solid State Ionics* **1999**, *118*, 311.

(4) Franke, M. E.; Simon, U. *ChemPhysChem* **2004**, *5*, 465.

(5) Franke, M. E.; Simon, U.; Moos, R.; Knezevic, A.; Muller, R.; Plog, C. *Physical Chemistry Chemical Physics* **2003**, *5*, 5195.

(6) Simon, U.; Flesch, U. *J. Porous Mater.* **1999**, *6*, 33.

(7) Wei, T.-C.; Hillhouse, H. W. *J. Phys. Chem. B* **2006**, *110*, 13728.